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Modelling of uranium extraction in sulphuric medium

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Abstract

A cationic extractant, 2-ethyl hexylphosphonic acid (PC88A), has been studied to recover uranium from conventional ore by solvent extraction. On the basis of experimental studies, extraction equilibria for uranium in sulphuric medium with PC88A were suggested.

Then, an extraction model was developed. Uranium speciation in the aqueous phase had to be established and the medium effects were taken into account according to the Specific Interaction Theory (SIT). Extraction equilibrium constants were determined by optimization. Thanks to this theory, the model does not depend on the experimental conditions and it was validated on a wide range of sulphate concentrations and acidities.

Keywords: uranium; solvent extraction; modelling; activity coefficients

1. Introduction

In the front end of the fuel cycle, conventional ores are leached by sulphuric acid. Then, a solvent extraction process is performed to recover uranium with a high purity. In the current extraction process, the organic reagent used is called Alamine 336, a mixture of tri-n-octyl/n-decylamine and it has not changed for 40 years. There are some drawbacks using Alamine, for example the coextraction of molybdenum, the main impurity, attenuates the

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extraction performances of the process. As a result, other reagents were studied to replace Alamine. Among the tested reagents, PC88A or 2-ethylhexyl 2-ethylhexyl phosphate exhibited good extraction performances ($(C_8H_{17})_2HPO_3$ c.f. Figure 1). In addition, this reagent is commercially available and is 20% cheaper than Alamine 336. This paper presents the experimental and modelling studies performed to achieve a better knowledge of uranium extraction mechanism.

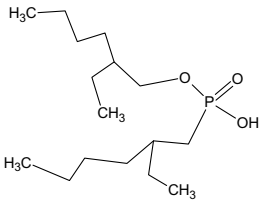

Fig. 1. Chemical formula for the extractant

Nomenclature

a_i	Activity of species i
A/O	Ratio of aqueous volume to organic volume
ESI-MS	ElectroSpray Ionisation Mass Spectrometry
HY	Acidic extractant (like PC88A)
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
I_m	Ionic strength
Ka*	Acido-basic apparent thermodynamic constant
$Ka^{I=0}$	Acido-basic thermodynamic constant at zero ionic strength
Kd	Dimerisation constant
K_{ex}	Extraction thermodynamic constant
m_i	Molality of species i
PC88A	2-ethylhexyl 2-ethylhexyl phosphate
SIT	Specific Interaction Theory
TPH	Hydrogenated TetraPropylene
Uorg	Uranium concentration in the organic phase after extraction
Uaq	Uranium concentration in the aqueous phase after extraction
z_i	Charge of ion i
β*	Complexation apparent thermodynamic constant
$\beta^{I=0}$	Complexation thermodynamic constant at zero ionic strength
γ_i	Activity coefficient of species i
ε	Interaction coefficient

2. Experimental

Batch solvent extraction experiments were performed in order to plot the distribution isotherm of uranium. The initial aqueous solution used for the extractions contained 2 $g.L^{-1}$ of uranium. Acidity was set at 0.2 M and sulphate concentration at 0.5 M. The organic phase consisted of 0.1 M of extractant diluted in hydrogenated tetrapropylene (TPH).

Ten extractions were performed by changing the ratio of aqueous volume to organic volume also called A/O ratio to load as much as possible the solvent with the extracted element. Analysis of this isotherm will enable an initial estimate of the stoichiometric coefficient of PC88A in the organic extracted complexes.

For all experiments, uranium and sulphate concentrations were measured by ICP-AES in the aqueous phase after extraction (also called raffinate). Acidity was determined by a potentiometric titration. These several analyses showed that uranium extraction did not change the sulphate concentration of the aqueous phase whereas the acidity was increased in a proportion to two hydrogens per uranium. As a result, uranium(VI) – UO_2^{2+} should be extracted by a cationic exchange mechanism, releasing protons in the aqueous phase.

For the extraction experiments, the uranium concentrations in the organic phase were estimated by mass balance.

PC88A is assumed to be in a dimeric form like most of the acidic extractants in non polar solvents. The dimerisation constant of PC88A in n-heptane was estimated to be Kd=3.10^3 L/mol by vapour pressure osmometry [1]. This means that the proportion of dimer is about 96 % with a concentration of PC88A of 0.1M. Although the diluent used is not the same, (the experiments were performed with TPH), we used the same dimerisation constant to build the model as these are two aliphatic diluents exhibiting weak interactions with the extractant.

Consequently, the extraction equilibrium is described by the following equation with $(HY)_2$ representing the dimerised form of PC88A:

$$UO_2^{2+} + i(\overline{HY})_2 \Leftrightarrow \overline{UO_2Y_2(HY)_{2(i-1)}} + 2H^+$$

The extraction isotherm showed that saturation of the organic phase seems to be reached with 11 $g.L^{-1}$ of uranium. Assuming that the extractant is completely dimerised in TPH, one mole of dimer is involved in the extraction equilibrium of uranium.

Meanwhile, a diluted sample of the organic phase from the extraction of uranium at a high A/O was analyzed by electrospray ionisation mass spectrometry (ESI-MS). This analysis suggested an extraction with two moles of dimer. Thus, both equilibria could occur for uranium extraction. Modelling will help to determine the predominance of each equilibrium.

3. Modelling

The extraction model of uranium was developed using the numerical calculation software Scilab©. The goal is to confirm the supposed chemical equilibria and to calculate their thermodynamic extraction constants.

Considering the following extraction equilibrium: $UO_2^{2+} + i(\overline{HY})_2 \Leftrightarrow \overline{UO_2Y_2(HY)_{2(i-1)}} + 2H^+$

The extraction constant is defined by:

$$K_{ex,i} = \frac{a\left(\overline{UO_2Y_2(HY)_{2(i-1)}}\right)a\left(H^+\right)^2}{a\left(\left(\overline{HY}\right)_2\right)^i a\left(UO_2^{2+}\right)} = \frac{\gamma_{UO_2Y_2(HY)_{2(i-1)}}\left[\overline{UO_2Y_2(HY)_{2(i-1)}}\right]\times\gamma_{H^+}^2\left[H^+\right]^2}{\gamma_{(\overline{HY})_2}^i\left[\left(\overline{HY}\right)_2\right]^i\times\gamma_{UO_2^{2+}}\left[UO_2^{2+}\right]}$$

In this equation, a(i) denotes the activity of species i, and γ_i its activity coefficient. In the organic phase, these coefficients are supposed to be almost constant whatever the considered composition and can be neglected. On the other hand, in the aqueous phase, the medium effects have to be taken into account. This is important to consider the deviation from ideality in this phase to be able to use the model on a wide range of acid and sulphate concentrations. That is why, the specific interaction theory (SIT) [2] [3] was used in this model.

The experiments presented before showed that only the cationic species of uranium UO_2^{2+} is extracted by PC88A. Consequently, uranium speciation in the aqueous phase had to be established as other species like $UO_2(SO_4)$, $UO_2(SO_4)_2^{2-}$, $UO_2(SO_4)_3^{4-}$ can be present in sulphuric medium.

Therefore, the extraction model of uranium is divided into three parts which are presented below:

- specific interaction theory (SIT)
- speciation
- extraction

3.1. Specific interaction theory (SIT)

According to SIT model, the activity coefficient γ_i of an ion i of charge z_i in the solution of ionic strength I_m may be described by the following equation:

$$\log \gamma_i = -z_i^2 D + \sum_j \varepsilon(i,j) m_j \quad with \quad D = \frac{A\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}}$$

A and B are constants which are temperature and pressure dependent, a_i is an ion size parameter for the hydrated ion i. At 25°C and 1 bar, A has a value of 0.509 $kg^{1/2}.mol^{-1/2}$ and Ba_i = 1.5 $kg^{1/2}.mol^{-1/2}$. The Debye-Hückel term D accounts for electrostatic long-range interactions whereas the ion interaction coefficient ε describes short range interactions between species. The summation in the equation extends over all ions j present in solutions.

The ionic strength is defined by: $I_m = \frac{1}{2}\sum_i z_i^2 m_i$. In synthetic leach solution, concentrations in the raffinates are comparable to their molalities (m_i) since the solution density is close to 1.

SIT theory is valid for ionic strength from 0.5 to 3.5 mol/kg and the ionic strength of genuine leach solutions has been determined to be around 1 mol/kg.

The part of the algorithm concerning SIT computes the ionic strength and activity coefficients of every species present in the aqueous solution. Consequently, it enables calculation of the complexation and acidity constants at the ionic strength of the solution from the equilibrium constants at zero ionic strength using the following equations:

$$\begin{cases} \beta_i^* = \beta_i^{I=0M} \times \dfrac{\left(\gamma_{SO_4^{2-}}\right)^i \gamma_{UO_2^{2+}}}{\gamma_{UO_2(SO_4)_i^{2(1-i)}}} = \dfrac{\left[UO_2(SO_4)_i^{2(1-i)}\right]}{\left[SO_4^{2-}\right]^i\left[UO_2^{2+}\right]} \\ Ka_i^* = Ka_i^{I=0M} \times \dfrac{\gamma_{H_iSO_4^{i-2}}}{\gamma_{H^+}\gamma_{H_{i-1}SO_4^{i-3}}} = \dfrac{\left[H^+\right]\left[H_{i-1}SO_4^{i-3}\right]}{\left[H_iSO_4^{i-2}\right]} \end{cases}$$

The star denotes apparent thermodynamic constants defined by the concentrations quotient instead of the activities quotient (the considered equilibria are referred in table 1).

3.2. Speciation

The chemical speciation of an element refers to all the chemical forms of an element in a given environment. The species present in the studied sulphuric aqueous solution are UO_2^{2+}, SO_4^{2-}, H^+, HSO_4^-, $UO_2(SO_4)$, $UO_2(SO_4)_2^{2-}$, $UO_2(SO_4)_3^{4-}$. The speciation part of the algorithm computes the activities of these species from the experimental data and from the complexation and acidity constants given by SIT.

The considered equilibria are reported below in Table 1.

Table 1. Complexation and acido-basic constants

Complexation equilibria	Constant	logβ at I=0 M
$UO_2^{2+} + SO_4^{2-} \leftrightarrow UO_2(SO_4)$	β_1	3.33
$UO_2^{2+} + 2SO_4^{2-} \leftrightarrow UO_2(SO_4)_2^{2-}$	β_2	4.29
$UO_2^{2+} + 3SO_4^{2-} \leftrightarrow UO_2(SO_4)_3^{4-}$	β_3	3.02
Acido-basic equilibria	**Constant**	**pKa at I=0M**
$H_2SO_4 \leftrightarrow H^+ + HSO_4^-$	Ka_2	-2
$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$	Ka_1	1.98

The mass balances in the aqueous phase regarded to the apparent constants are:

$$\begin{cases} [U] = [UO_2^{2+}] \times \left(1 + \beta_1^* [SO_4^{2-}] + \beta_2^* [SO_4^{2-}]^2 + \beta_3^* [SO_4^{2-}]^3\right) \\ [S] = [SO_4^{2-}] + \dfrac{[H^+][SO_4^{2-}]}{Ka_1^*} + \dfrac{[H^+]^2[SO_4^{2-}]}{Ka_1^* Ka_2^*} + \beta_1^* [UO_2^{2+}][SO_4^{2-}] + 2\beta_2^* [UO_2^{2+}][SO_4^{2-}]^2 \\ \qquad + 3\beta_3^* [UO_2^{2+}][SO_4^{2-}]^3 \\ [H] = [H^+] + \dfrac{[H^+][SO_4^{2-}]}{Ka_1^*} + 2 \times \dfrac{[H^+]^2[SO_4^{2-}]}{Ka_1^* Ka_2^*} \end{cases}$$

The algorithm is based on the solving of the mass balance on each element: H, S, U.

3.3. Extraction

Extraction equilibrium constants are determined by minimizing the root mean square deviation between calculated and experimental organic concentrations.

The organic concentration of uranium is calculated according to the formulae:

$$\left[\overline{UO_2 Y_2 (HY)_{2(i-1)}}\right] = \frac{K_{ex,i} \times \left[\overline{(HY)_2}\right]^i \times \gamma_{UO_2^{2+}} \left[UO_2^{2+}\right]}{\times \gamma_{H^+}^2 \left[H^+\right]^2}$$

The free concentration of extractant $\left[\overline{HY}\right]$ and consequently the free concentration of dimer $\left[\overline{(HY)_2}\right]$ are determined by a mass balance on the organic phase:

$$[\overline{HY}]_{ini} = [\overline{HY}] + 2\left[\left(\overline{HY}\right)_2\right] + \sum_i 2i\left[\overline{UO_2Y_2(HY)_{2(i-1)}}\right]$$

$$= [\overline{HY}] + 2 \times Kd \times [\overline{HY}]^2 + \sum_i 2i \times \frac{K_{ex,U,i} \times a\left(UO_2^{2+}\right) \times Kd^i \times [\overline{HY}]^{2i}}{a\left(H^+\right)^2}$$

3.4. Results

Optimization was performed with the distribution isotherm data.

Different chemical equilibria were tested. The best agreement between experimental and calculated uranium organic concentrations was obtained by considering the following two equilibria:

$$\begin{cases} UO_2^{2+} + \overline{(HY)_2} \leftrightarrow \overline{UO_2Y_2} + 2H^+ \quad (K_{ex1}) \\ UO_2^{2+} + 2\overline{(HY)_2} \leftrightarrow \overline{UO_2(HY_2)_2} + 2H^+ \quad (K_{ex2}) \end{cases}$$

The calculated extraction constants are log Kex_1 = 3.06 and log Kex_2 = 3.98 and the average relative deviation between the calculated and the experimental values is 6.1%.

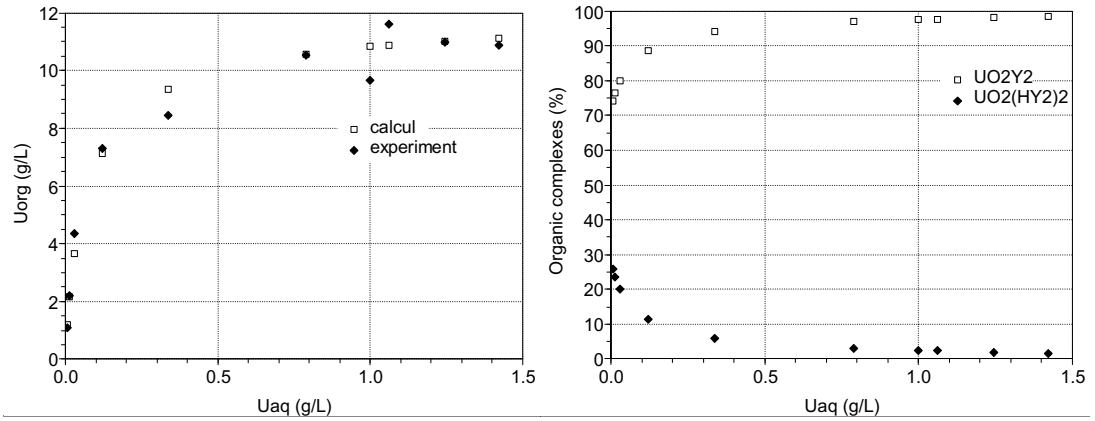

Fig. 2. (a) Calculated and experimental distribution isotherms of uranium; (b) Species distribution in the organic phase

Considering these equations associated to its optimized constants it is possible to calculate the proportion of each complex for different solvent saturation (Figure 2.b). In the saturated solvent, $\overline{UO_2Y_2}$ is the predominant complex, it is the complex found with saturation data. Away from saturation, $\overline{UO_2\left(HY_2\right)_2}$ represents around 30% of the complexes formed, it is the complex found with ESI-MS analyzes.

3.5. Model validation at other experimental conditions

Extractions were performed at different experimental conditions. Acidity was set at 0.2 and 0.5 M and sulphate concentration between 0.3 and 1.2 M. The extraction model of uranium was tested in these conditions using the extraction constants calculated in the previous part. It was observed that the calculated values matched the experimental values. The average relative deviation for the new data is less than 10%.

4. Conclusion

Experimental work is the first step to understand extraction mechanisms. Unlike Alamine 336, the uranium distribution isotherm showed that UO_2^{2+} is extracted by a cation exchange mechanism. This information is important for the process as this means that increasing acidity will decrease uranium extraction. The equilibria which enable simulation of uranium behaviour are:

$$\begin{cases} UO_2^{2+} + \overline{(HY)_2} \leftrightarrow \overline{UO_2Y_2} + 2H^+ \quad (\log K_{ex1} = 3.09) \\ UO_2^{2+} + 2\overline{(HY)_2} \leftrightarrow \overline{UO_2(HY_2)_2} + 2H^+ \quad (\log K_{ex2} = 3.98) \end{cases}$$

Thanks to SIT theory, the uranium extraction model does not depend on these experimental conditions and it was validated on a wide range of sulphate concentrations (from 0.3 to 1.2 M) and acidities (from 0.2 to 0.5M).

The extraction equilibria were implemented into the PAREX code developed by the CEA [4], which enables the simulation of counter current solvent extraction operations. The use of PAREX will allow the development and the optimization of a new efficient process dedicated to uranium extraction for conventional ores.

Acknowledgement

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